

ELECTROLYTE AND ELECTRODE PASSIVATION FOR THIN FILM BATTERIES

W. C. West, J. F. Whitacre, B. V. Ratnakumar, E. Brandon, J. O. Blosiu and S. Surampudi

Electrochemical Technologies Group,
Center for Integrated Space Microsystems
Jet Propulsion Laboratory
California Institute of Technology
Pasadena CA 91109

ABSTRACT

Passivation films for thin film batteries have been prepared and the conductivity and voltage stability window have been measured. Thin films of Li_2CO_3 have a large voltage stability window of 4.8V, which facilitates the use of this film as a passivation at both the lithium anode-electrolyte interface at high cathodic potentials. The ionic conductivity of the Li_2CO_3 films are rather low, 5×10^{-9} S/cm, which may be due to the nanocrystalline texture of the sputtered thin films. Sputtered films of Li_2CO_3 show evidence of Li_2O incorporation, which affects the air stability of the films. Sputtering at higher power levels attenuates the Li_2O , thus improving air stability of the as-deposited films.

INTRODUCTION

The selection of materials for Li thin film batteries involve similar concerns associated with conventional Li batteries; in particular, selection of a suitable electrolyte with stability versus lithium or oxidation at high potentials. In contrast to conventional batteries, the preparation techniques used to prepare thin film batteries offer distinct advantages over conventional battery fabrication by allowing for the engineering of cells with multi-layer components without a significant increase in the complexity of fabrication. For example, as demonstrated by Jones and Akridge,¹ a thin film electrolyte structure may be fabricated with a high ionic conductivity material coated with a material with high stability versus Li. In this example, though, the use of LiI as a buffer layer was limited to low potentials given the relatively narrow voltage stability window of LiI. The development of films that can provide stability at both anode and cathode potentials enables the use of many previously unusable electrolyte materials with poor chemical or electrochemical stability, and eases the developmental constraints on novel electrolytes.

Thin films of sputtered Li_2CO_3 have been examined as passivation layers for thin film batteries due to the advantages compared to other passivation layers, including:

- Excellent passivation against electrolyte reaction at the anode²
- Excellent oxidative stability at high voltage as evidenced by the oxidative stability of carbonate-based liquid electrolytes up to 4.8V³
- Good stability against humidity in air⁴

The latter advantage is quite important in practical terms, since air stable components of a thin film battery will be much less expensive to process using conventional microfabrication tools in ambient air, compared with air sensitive materials.

Furthermore, the preparation of thin films of Li_2CO_3 is of interest since to the best of our knowledge, no reports of sputtered thin films of Li_2CO_3 have been published. Although bulk polycrystalline Li_2CO_3 is known to be a rather low ionic conductor at room temperature, the conductivity of thin films are often significantly better ionic conductors than the bulk electrolyte material. Also, it is of interest whether thin films of Li_2CO_3 can be nitrified when sputtered in a N_2 ambient with associated improvements in conductivity and voltage stability as with Li_3PO_4 ,⁵ or with improvements in air stability as with LiBO_2 .⁶

EXPERIMENTAL

All Li_2CO_3 films were prepared by RF magnetron from a 3" target. The films were deposited on a variety of substrates, depending upon the measurement technique to be employed. No active substrate cooling was used, so an increase in the substrate temperature from the plasma was observed, though the temperature increase was estimated to be no more than 50°C above ambient temperature.

The Li_2CO_3 target was fabricated by melting Li_2CO_3 powder (Aldrich Chemicals) in air at 700°C and then quickly pouring the melt into a 3" target mold. The solidified target was then sanded flat on both sides and clamped to an aluminum backing plate. Care was taken to minimize the time the Li_2CO_3 melt was held at 700°C since decomposition of the melt to CO_2 and Li_2O can occur at or above the melting temperature.⁷

The applied RF power level was varied between 75 and 200 W. Various sputter gas stoichiometries were examined, though primarily a 10:1 molar ratio $\text{CO}_2:\text{O}_2$ ambient was used for most experiments to shift the equilibrium of the decomposition reaction to a reactant-rich state. The total gas flow was kept constant at 56 sccm, and the operating pressure was held at 10 mTorr.

Film phase content, crystallography, and structure were examined using x-ray diffraction experiments conducted at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 2-1. The extremely intense x-rays produced at SSRL were necessary to attain adequate signal to noise ratios in scattered intensities from the thin Li_2CO_3 films, whose constituent atoms had extremely low atomic scattering factors. This problem was compounded by the fact that crystalline Li_2CO_3 has a low-symmetry monoclinic structure, giving a diffraction pattern with many low intensity maxima. The x-ray radiation was tuned to 8 keV using a (111) Si monochromator. Both the θ - 2θ and asymmetric grazing incidence geometries were used to collect the data.

X-ray photoelectron spectroscopy was used to examine film composition and local electronic structure. A PHI 550 ESCA system was used with Al $K\alpha$ radiation. An ion gun (2 keV Ar) was used to clean the surface. The 1s transitions of O, C, and Li were all evident and allowed for compositional quantification using the peak area method.⁸

The electrical characterization of the films was performed using a Solartron 1250/1286 FRA/potentiostat. The applied AC signal for the impedance spectroscopy measurements was 20 mV, with frequency between 65000 – 0.5 Hz. The DC potentiodynamic measurements were performed at 1mV/sec sweep rates between 0-6V.

RESULTS AND DISCUSSION

Li_2CO_3 sputtered films were nanocrystalline, with Li_2CO_3 grain size on the order of 10-20 nm, as evidenced by the diffraction patterns shown in Figure 1. The films show modest changes in texturing, grain size, and phase content when sputtered in differing sputter gas ambients. The nanocrystalline nature of the films is confirmed by a transmission electron microscopy study. Li_2CO_3 films sputtered on thin carbon grids show evidence of crystalline grains on the order of 10 nm as shown in the light and dark field TEM images, Figures 2A and 2B respectively.

The electrical characteristics of the Li_2CO_3 films are typical of a solid electrolyte-double blocking electrode sample, as shown in Bode plot in Figure 3. The equivalent circuit used to fit the experimental data is the model proposed by Yu et al.⁵ for Pt|Lipon|Pt (Figure 4). The conductivity of the electrolyte was determined from the real component of the impedance at a local minima in the imaginary component of impedance.⁹ The room temperature conductivity of the Li_2CO_3 films is rather low, approximately 5×10^{-9} S/cm. The conductivity can be fit to an Arrhenius activation, with a relatively low activation energy of approximately 0.35 eV, shown in Figure 5.

The voltage stability window of Li_2CO_3 was determined to be approximately 4.8V. Figure 6 shows breakdown characteristics of the films. The DC properties of the films in the Li| Li_2CO_3 |Mo were also characterized. The films show no evidence of formation of a growing reaction layer at the Li| Li_2CO_3 interface, and have stable impedance spectra over several hours. Thus, the films may be used as passivation films at both high oxidative potentials and in contact with lithium.

As a means of comparison to a baseline electrolyte of Lipon, the DC characteristics of Lipon was also studied. As shown in Figure 7, typical Lipon films broke down between 5-5.5V, in reasonably good agreement with others.⁵ However, in contrast to the Li_2CO_3 films, the background current of the Lipon films before breakdown was roughly 0.2 μA . The Li_2CO_3 films beyond 2 V exhibited significant background current on the order of 2 μA . The origin of this background current is likely due to the presence of Li_2O in the as-deposited films. Figure 8 represents X-ray photoelectron spectroscopy data, indicating that the samples are 35-50 mol% Li_2O in Li_2CO_3 . Based on these data, it is likely that the background current observed in the DC voltametry scan is due to the breakdown of Li_2O .

The appearance of Li_2O in the Li_2CO_3 films is not surprising given the decomposition pathway for Li_2CO_3 to Li_2O and CO_2 . Qualitatively, a trend for increasing air stability with increasing applied RF power was observed. The air stability of the samples was attributed to the content of hygroscopic Li_2O in the sputtered films. Samples prepared at 75 W underwent obvious morphology changes, in terms of roughening and hazing, almost immediately in humid air. The electrical characteristics of these films were also quite unstable with time. Samples prepared at 200 W, however, were air stable for several days, with little change in morphology and electrical properties. Virtually no change in the electrical properties of the film could be observed when films were sputtered in N_2 .

In addition to work performed on Li_2CO_3 as a passivation film, other materials were considered as well. LiF is air stable and much less hygroscopic than other Li halides, and has a suitably wide voltage stability window. However, LiF is a very poor ionic conductor. Li_3PO_4 is air stable and non-water reactive when sputtered in Ar/ O_2 , but is known to also have low conductivity and a voltage stability of about 3.5 V.⁵ In light of previous reports of improved conductivity of LiPO_3 with additions of LiF,¹⁰ a mixture of 0.67 : 0.33 mol Li_3PO_4 -LiF was examined for conductivity and voltage stability. The

impedance spectrum revealed multiple relaxations (Figure 9), indicative of a phase separated material.¹¹ The voltage stability was determined to be nearly identical to Li_3PO_4 films, as well (Figure 10). Unfortunately, little enhancement in ionic conductivity of Li_3PO_4 films could be obtained with addition of LiF to the Li_3PO_4 target.

CONCLUSIONS

Films of Li_2CO_3 have been prepared and the properties reported for the first time. Ionic conductivity and the voltage stability window have been determined for Li_2CO_3 based films. Although the voltage stability window is large enough to facilitate use of these films at both the Li anode-electrolyte and the cathode-electrolyte interface, the conductivity is rather low, limiting the usable thickness of these films as passivation layers.

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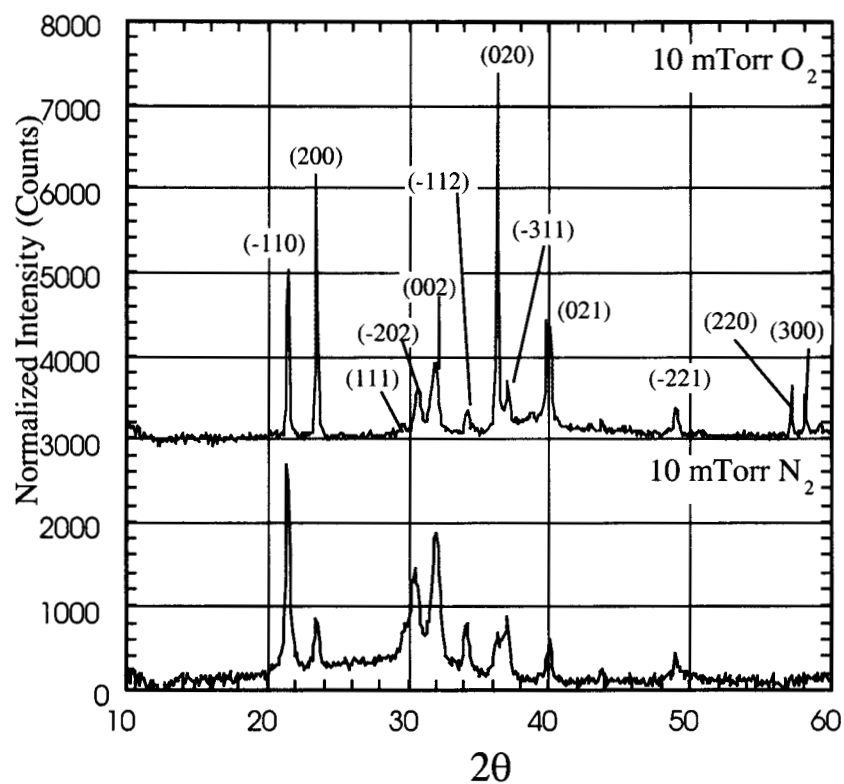


Figure 1. Diffraction patterns of Li_2CO_3 films sputtered in O_2 and N_2 .

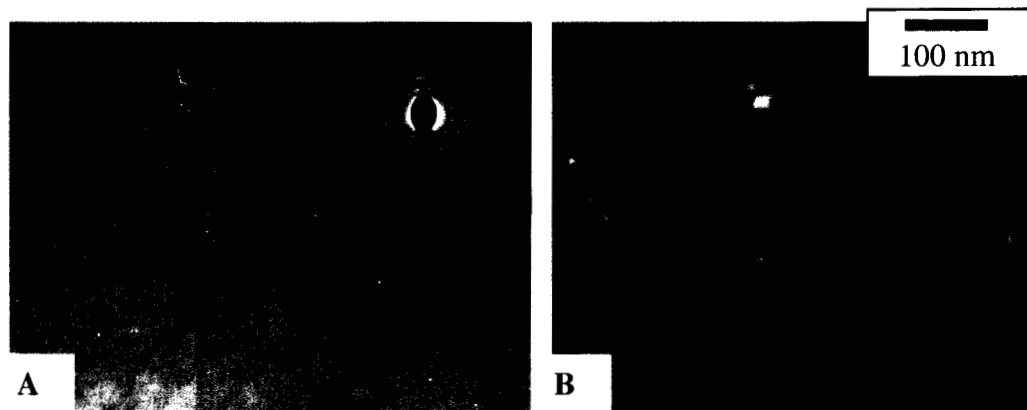


Figure 2. Light field (A) and dark field (B) transmission electron micrographs of Li_2CO_3 sputtered on carbon grids.

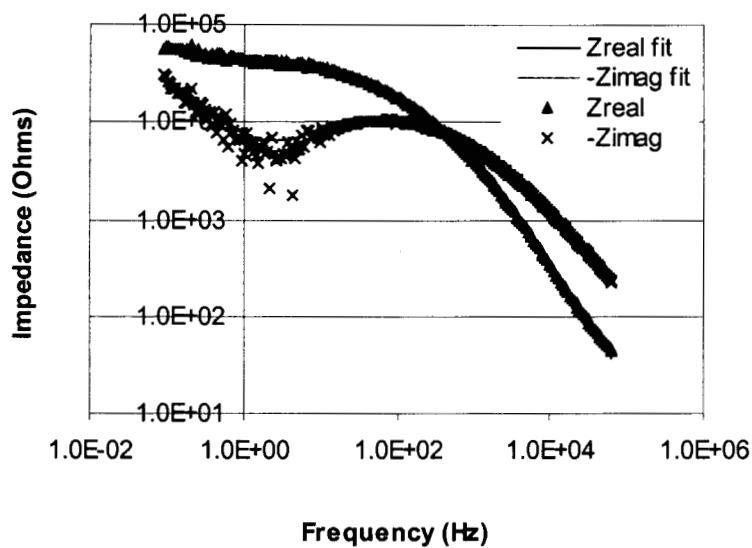


Figure 3. Bode plot of a Mo|Li₂CO₃|Mo sample.

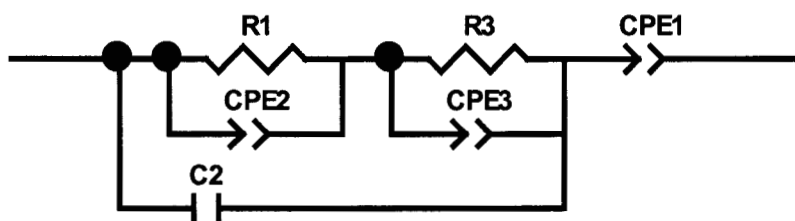


Figure 4. Equivalent circuit used to model the Mo|Li₂CO₃|Mo cell.⁵

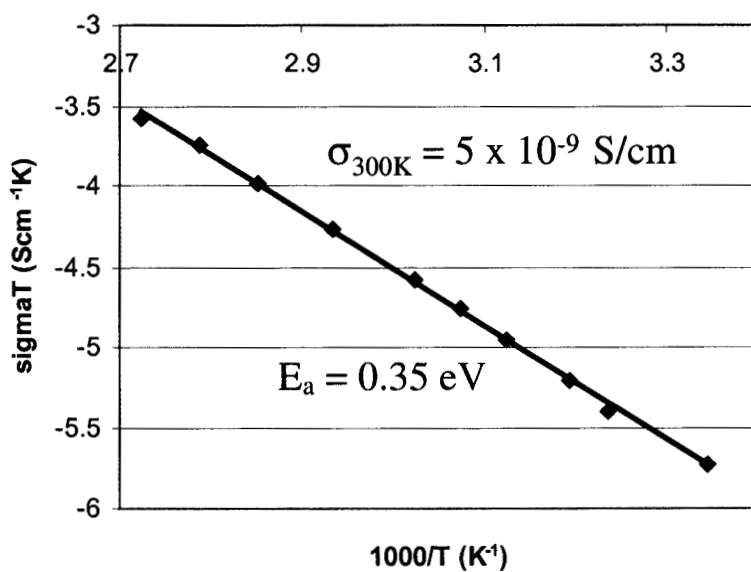


Figure 5. Arrhenius plot of the conductivity of Li₂CO₃ films.

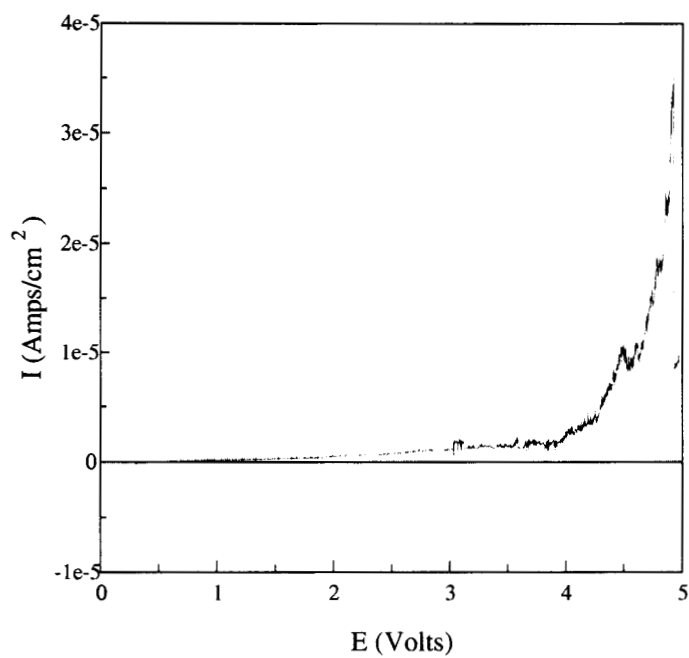


Figure 6. DC breakdown characteristics of Mo|Li₂CO₃|Mo cell.

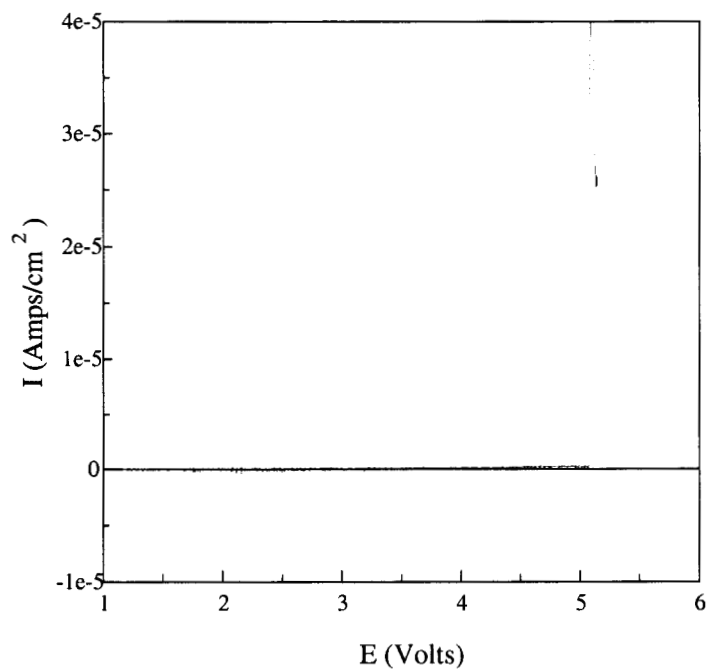


Figure 7. DC breakdown characteristics of Mo|Lipon|Mo cell.

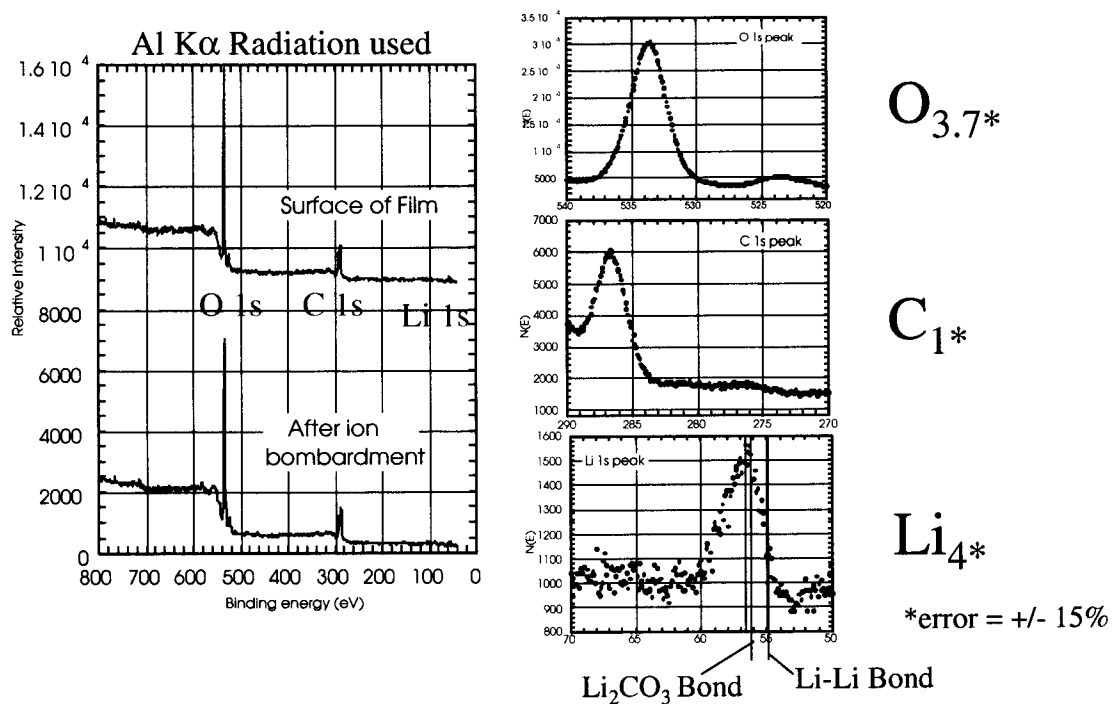


Figure 8. X-ray photoelectron spectroscopy data. The apparent ratio of Li₂O to Li₂CO₃ is 35-50 mol%.

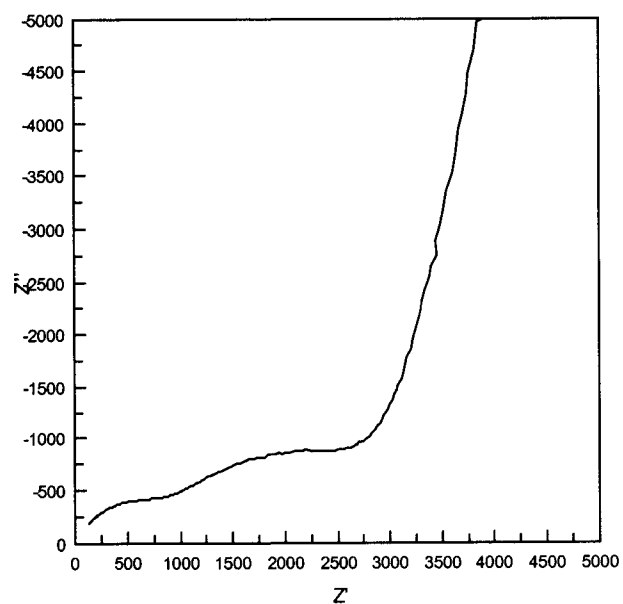


Figure 9. Complex plane plot of 0.67:0.33 mol Li₃PO₄: LiF films.

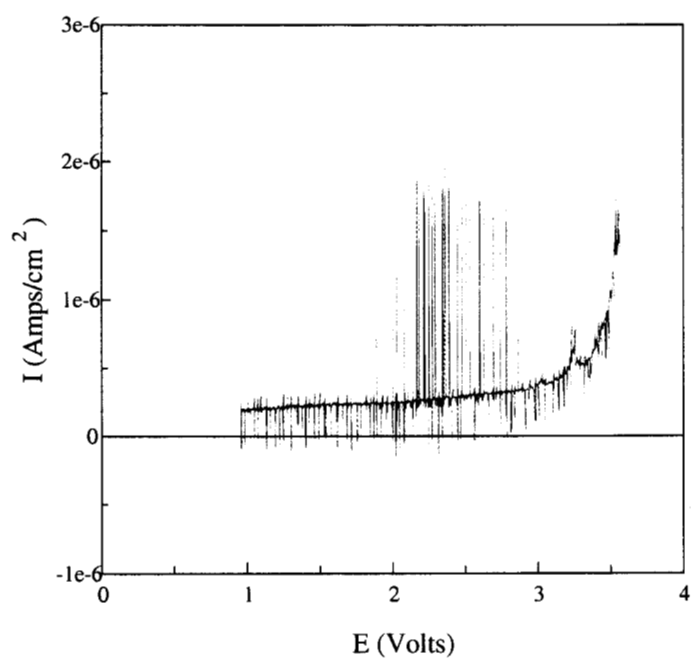


Figure 10. DC breakdown characteristics of 0.67:0.33 mol Li_3PO_4 : LiF films.